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MATHEMATICAL MODELING OF THE RHEOLOGY OF SWELLING SYSTEMS

N. B. Pleshchinskii, M. G. Khramchenkov,
and É. M. Khramchenkov

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Consideration is given to a mathematical model of the rheology of swelling systems, the basis for which is provided by generalization of the filtration-consolidation theory to the case where the mass of the solid phase of a porous skeleton changes due to the flow of a fluid during the swelling and shrinkage processes under the action of osmotic pressure. The problem on swelling and shrinkage of a clay layer has been formulated and solved. The features of the model, which are important for explanation of certain characteristic features of the processes in swelling systems, have been investigated based on an analysis of the solution. It has been shown that the solutions obtained are in good agreement with experimental results.

Introduction. Swelling systems are traditionally an object of close attention and investigation in physicochemical mechanics, biomechanics and biophysics, polymer physics, hydrogeology, and a number of other branches. Examples of swelling systems in nature are provided by soils, clay rocks, certain polymers, and polymolecular systems of living organisms. The mechanics of such systems is usually constructed based on empirical rheological models saying little about the physical nature of swelling in them. There is a necessity of combining purely mechanical concepts of the processes in swelling systems with the physicochemical properties (common to both inorganic and organic objects) of such systems. In our opinion, osmotic pressure in swelling systems, which is a motive force for the process of swelling, can be a property of this kind. This pressure induces flow of a fluid to (from) a solid matrix and causes the additional stresses finally arresting the swelling to appear. Therefore, the swelling matrix may be considered as a porous medium with a swelling skeleton. As a model describing the mechanics of such systems, we may select the thoroughly studied filtration-consolidation model [1], but the latter must be generalized to the case of the porous skeleton of variable mass. Swelling thermodynamics has been presented in a number of monographs, of which we use [2].

Physicochemical Mechanics of Swelling Systems. We write the basic mechanical equations for swelling systems. For the mass of the liquid phase and the mass of the skeleton material, the balance equations have the form

$$\frac{\partial m\rho_f}{\partial t} + \mathrm{div}\,(m\rho_f \mathbf{V}_f) + j = 0\,, \quad \rho_f = \mathrm{const}\,, \tag{1}$$

$$\frac{\partial\,(1-m)\,\rho_s}{\partial t} + \mathrm{div}\,[(1-m)\,\rho_s \mathbf{V}_s] - j = 0\,, \quad \rho_s \neq \mathrm{const}\,. \tag{2}$$

The mass of the representative element of volume V_0 of the porous medium will be written as

$$M_s = \rho_s^0 V_s^0 + \rho_f \left[(1-m)\,V_0 - V_s^0\right], \quad V_s^0\,, \quad \rho_s^0 = \mathrm{const}\,. \tag{3}$$

From expression (3), for the skeleton-material density we have

$$\rho_s = \frac{M_s}{(1-m)\,V_0} = \frac{\varepsilon V_s^0}{(1-m)\,V_0} + \rho_f\,, \quad \varepsilon = \rho_s^0 - \rho_f\,. \tag{4}$$

Kazan' State University, 17, Universitetskaya Str., Kazan', 420008, Russia; email: Maxim.Khramchenkov@ksu.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 6, pp. 93–99, November–December, 2005. Original article submitted March 19, 2004.

Dividing Eqs. (1) and (2) by ρ_f and adding the results together, with account for (4) we obtain

$$\mathrm{div}\,\frac{\kappa\mathbf{V}_\mathrm{s}}{V_0}+\mathrm{div}\,\mathbf{q}+\mathrm{div}\,\mathbf{V}_\mathrm{s}+\frac{\partial}{\partial t}\left(\frac{\kappa}{V_0}\right)=0\,. \tag{5}$$

As a result of determination of the shrinkage $dV_0/V_0 = d\vartheta$ and introduction of the notation $\varepsilon V_\mathrm{s}^0/\rho_\mathrm{f} = \boldsymbol{\kappa}$ and $\mathbf{q} = m(\mathbf{V}_\mathrm{f} - \mathbf{V}_\mathrm{s})$, Eq. (5) is easily transformed to the form

$$\mathrm{div}\,\mathbf{q}+\kappa a e^{-\vartheta}\,(-\,\mathbf{V}_\mathrm{s}\nabla\vartheta+\mathrm{div}\,\mathbf{V}_\mathrm{s})+\mathrm{div}\,\mathbf{V}_\mathrm{s}-a\kappa e^{-\vartheta}\,\frac{\partial\vartheta}{\partial t}=0\,,\quad V_0=V_0^{(0)}e^{\vartheta}\,,\quad a=1/V_0^{(0)}\,. \tag{6}$$

It is clear that $\mathbf{V}_\mathrm{s}\nabla\vartheta \to 0$ as a second-order infinitesimal; then (6) yields

$$\mathrm{div}\,\mathbf{q}+\mathrm{div}\,\mathbf{V}_\mathrm{s}+\kappa a e^{-\vartheta}\left(\mathrm{div}\,\mathbf{V}_\mathrm{s}-\frac{\partial\vartheta}{\partial t}\right)=0\,. \tag{7}$$

Determining $\mathrm{div}\,\mathbf{V}_\mathrm{s} = \partial\vartheta/\partial t$, from (7) we finally obtain

$$\mathrm{div}\,\mathbf{q}+\frac{\partial\vartheta}{\partial t}=0\,. \tag{8}$$

We write the momentum-balance equation in the form of the equilibrium equation

$$G_{ij}=(1-m)\,\sigma_{ij}^\mathrm{s}-mp\delta_{ij}=(1-m)\,(\sigma_{ij}^\mathrm{s}+p\delta_{ij})-p\delta_{ij}\,,$$

which, after the introduction of the notation $(1-m)(\sigma_{ij}^\mathrm{s}+p\delta_{ij}) = \sigma_{ij}^\mathrm{f}$, will take a form traditional for the filtration-consolidation theory:

$$G_{ij}=\sigma_{ij}^\mathrm{f}-p\delta_{ij}\,. \tag{9}$$

Let us turn to the energy-balance equation. We write the first and second laws of thermodynamics:

$$\left.\begin{array}{l} dU_\mathrm{s}=\delta Q^{(\mathrm{e})}+\delta A^{(\mathrm{i})} \\ TdS_\mathrm{s}=\delta Q^{(\mathrm{e})}+\delta Q'\,,\quad \delta Q'\geq 0 \end{array}\right\}\Rightarrow \delta A^{(\mathrm{i})}=dU_\mathrm{s}-\delta Q^{(\mathrm{e})}=dF_\mathrm{s}+\delta Q'\,. \tag{10}$$

In accordance with the living-force theorem, for the case where the action of mass forces is absent we have

$$\frac{\delta A^{(\mathrm{i})}}{dt}=\int\limits_{V_\mathrm{s}}\sigma_{ij}^\mathrm{s}\,\frac{\partial U_i}{\partial x_j}\,dV=\int\limits_{V_\mathrm{s}}\frac{\partial}{\partial x_j}\,(U_i\sigma_{ij}^\mathrm{s})\,dV=\int\limits_{\Sigma_\mathrm{s}}\sigma_{ij}^\mathrm{s}n_jU_idS=\int\limits_{S_\mathrm{s}^\mathrm{e}}\sigma_{ij}^\mathrm{s}n_jU_idS+\int\limits_{\Sigma_\mathrm{s-f}}-pn_iU_idS=$$

$$=\int\limits_{S_\mathrm{s}^\mathrm{e}}\tau_{ij}^\mathrm{s}n_jU_idS+\int\limits_{S_\mathrm{s}^\mathrm{e}}(-\,\sigma^\mathrm{f}+p)\,n_iU_idS+\int\limits_{\Sigma_\mathrm{s}}-pn_iU_idS\,,\quad \sigma^\mathrm{f}=-\frac{1}{3}\,\sigma_{ii}^\mathrm{f}\,. \tag{11}$$

Passage to the values averaged over the representative volume in (11) yields

$$\frac{\delta A^{(\mathrm{i})}}{dt}=\int\limits_{\partial V_0}(1-m)\,\langle\tau_{ij}\rangle\,\langle U_i\rangle\,n_jdS_0+\int\limits_{\partial V_0}(1-m)\,\langle-\,\sigma+p\rangle\,\langle U_i\rangle\,n_idS_0+\int\limits_{\Sigma_\mathrm{s}}-pU_in_idS\,. \tag{12}$$

We introduce the definition of the effective-stress tensor

$$\sigma^{\mathrm{f}}_{ij} = T_{ij} - \sigma^{\mathrm{f}}\delta_{ij} = (1 - m)\,(\langle\tau^{\mathrm{s}}_{ij}\rangle - \langle\sigma - p\rangle\,\delta_{ij})$$

and write (12) in the form

$$\frac{\delta A^{(\mathrm{i})}}{dt} = \int_{V_0} \frac{\partial}{\partial x_j}\,(\sigma^{\mathrm{f}}_{ij}\,\langle U_i\rangle)\,dV + \int_{\Sigma_{\mathrm{s}}} - pU_n dS = V_0\sigma^{\mathrm{f}}_{ij}e_{ij} + \int_{\Sigma_{\mathrm{s}}} - pU_n dS\,, \tag{13}$$

where

$$\int_{\Sigma_{\mathrm{s}}} - pU_n dS = - p\int_{\Sigma_{\mathrm{s}}} U_n dS = - p\dot{V}_{\mathrm{s}} = - p\,\frac{\partial}{\partial t}\,[(1 - m)\,V_0] = pV_0\dot{m} - p\,(1 - m)\,\dot{V}_0\,.$$

Taking into account that $\dot{V}_0 = V_0\dot{\vartheta}$, we obtain

$$\int_{\Sigma_{\mathrm{s}}} - pU_n dS = V_0 p\dot{m} - p\,(1 - m)\,V_0\dot{\vartheta}\,. \tag{14}$$

Next we consider the situation where the skeleton proper manifests its elastic properties. This holds true of small strains, as the experiment shows, but fails for large strains. In this case, from (13) and (14), we have

$$\frac{\delta Q'}{dt} = 0 \Rightarrow \frac{1}{V_0}\,\dot{F}_{\mathrm{s}} = \sigma^{\mathrm{f}}_{ij}e_{ij} + p\dot{m} - p\,(1 - m)\,\dot{\vartheta}\,. \tag{15}$$

Since the free energy is, generally speaking, the function $F_{\mathrm{s}} = F_{\mathrm{s}}\,(J_2', \vartheta, m)$, we have

$$\dot{F}_{\mathrm{s}} = 2\,\frac{\partial F}{\partial J_2'}\,\varepsilon'_{ij}e'_{ij} + \frac{\partial F}{\partial\vartheta}\,\dot{\vartheta} + \frac{\partial F}{\partial m}\,\dot{m}\,. \tag{16}$$

Expressions (15) and (16) yield that

$$- p\,(1 - m) + \sigma^{\mathrm{f}} = \frac{\partial F}{\partial\vartheta}\,, \quad T_{ij} = 2\,\frac{\partial F}{\partial J_2'}\,\varepsilon'_{ij}\,, \quad \frac{\partial F}{\partial m} = p\,.$$

Setting $F = \frac{\lambda}{2}\,\vartheta^2 + \mu J_2' - \nu\vartheta\sqrt{J_2'}$ in accordance with [3] and assuming that $m << 1 \Rightarrow m \approx$ const, we finally obtain

$$- [p\,(1 - m) - \sigma^{\mathrm{f}}] = \lambda\vartheta - \nu\sqrt{J_2'}\,, \quad T_{ij} = (2\mu - \nu\vartheta/\sqrt{J_2'})\,\varepsilon'_{ij}\,. \tag{17}$$

Equations (17) play the role of rheological relations. It is noteworthy that the first equation of (17) together with (9) enable us to explain the appearance of abnormally high pressures of the fluid in the bed with a swelling skeleton [4].

Swelling Dynamics. Let us consider the process of swelling in greater detail. In discussions, we will rely on the concept (developed by one author in [5]) of an osmotic cell, in accordance with which the osmotic pressure is found, under equilibrium conditions, from the equality of the chemical ionic potentials of the solution within the solid skeleton and the solution in transport pores:

$$\mu_k = \bar{\mu}_k\,, \quad k = 1, 2\,. \tag{18}$$

Selecting as an example for calculation a 1 – 1 electrolyte (the cations and anions have a charge of 1 in the units of elementary charge of the corresponding sign) and using the standard representation for the form of chemical potential, we obtain

$$\mu_k = \mu_k^0 (p, T) + RT \ln C_k + ez_k\Phi \,, \quad z_k = \pm 1 : \quad C_1C_2 = C^2 = \overline{C}_1\overline{C}_2 \,. \tag{19}$$

The last equation in (19) represents the condition of Donnan equilibrium [2]. However, the system of equations (19) is open. To close it we use the condition of electroneutrality of the solid skeleton phase–pore solution system:

$$(\overline{C}_1 - \overline{C}_2)\,[(1 - m)\,V_0 - V_s] = e \,, \quad e' = e/[(1 - m)\,V_0 - V_s] \,. \tag{20}$$

Physically Eq. (20) means that the solid skeleton particles carry an excess (negative for the sake of definiteness) electric charge. This charge is compensated for with the pore-solution cations, so we have an excess of the cations as compared to the pore-solution anions, which causes the osmotic forces to appear. The entire scenario described is true of such swelling systems as clays and of some others. The solution of Eqs. (19) with account for (20) is as follows:

$$\overline{C}_1 = \frac{e'}{2} + \sqrt{\frac{e'^2}{4} + C^2} \,, \quad \overline{C}_2 = -\frac{e'}{2} + \sqrt{\frac{e'^2}{4} + C^2} \,. \tag{21}$$

Then, from (21), for the osmotic pressure we have the dependence

$$\pi = \frac{RT}{2}\left(\sqrt{e'^2 + 4C^2} - 2C\right), \tag{22}$$

which is transformed as follows when $C = 0$:

$$\pi = \frac{1}{2}\,RTe' = \frac{1}{2}\,\frac{RTe}{(1 - m)\,V_0 - V_s} \,. \tag{23}$$

The skeleton particles are affected by two forces — the osmotic pressure in the pore solution and the effective stress preventing swelling. It is clear that their difference is the resultant force leading to either swelling or shrinkage. Thus, the equation of swelling is rationally written in the form

$$\frac{\partial}{\partial t}\,[V_s\,(\rho_s - \rho_w) + (1 - m)\,\rho_w V_0] = \alpha\,[(1 - m)\,\pi - \sigma^f] \,. \tag{24}$$

Dependence (24) describes the dynamics of change in the skeleton mass due to the inflow (forcing through) of water during the swelling (shrinkage). Equations (23) and (24) close the general system of mechanical equations for the process of swelling (shrinkage).

Rheological Properties of Swelling Systems. We investigate the rheology of swelling systems using the one-dimensional problem of swelling and shrinkage of a layer under the action of a constant load applied to it as an example. Formulation of the problem follows from Eqs. (8), (9), (17), (20), (23), and (24) supplemented with Darcy's law for the filtration rate and with the determination of swelling and shrinkage:

$$\Gamma = \sigma^f + p \,, \quad \Gamma = \text{const} \,, \tag{25}$$

$$(1 - m)\,p + \sigma^f = -\,\varphi\,(\vartheta) \,, \tag{26}$$

$$\dot{\vartheta} + \frac{\partial q}{\partial z} = 0 \,, \tag{27}$$

$$q = -\left(\frac{k}{\eta}\right)\frac{\partial p}{\partial z} \,, \quad k = k_0 + Bm \,, \quad k_0, B = \text{const} \,, \tag{28}$$

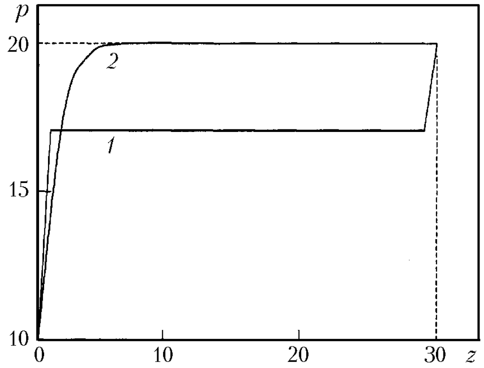


Fig. 1. Pressure profile in the layer (stationary stage): 1 and 2) conditions of the first and second kind at the right-hand boundary of the layer. p, kPa; z, cm.

$$V_0 = V_0^{(0)} \exp \vartheta \,, \tag{29}$$

$$\frac{\partial}{\partial t}\left[V_s (\rho_s - \rho_w) + \rho_w (1 - m) V_0\right] = \alpha \left[(1 - m) \pi - \sigma^f\right], \tag{30}$$

$$\pi = \frac{0.5eRT}{(1 - m) V_0 - V_s} \,. \tag{31}$$

Thus, the sought functions of the system of equations (25)–(31) are σ^f, p, ϑ, m, k, q, V_0, and π; the constants of the model are Γ, η, k_0, $V_0^{(0)}$, ρ_w, ρ_s, e, α, R, and T. The boundary conditions have the form

$$p \,|_{z=z_0} = \Gamma \,, \;\; p \,|_{z=0} = p_0 \tag{32}$$

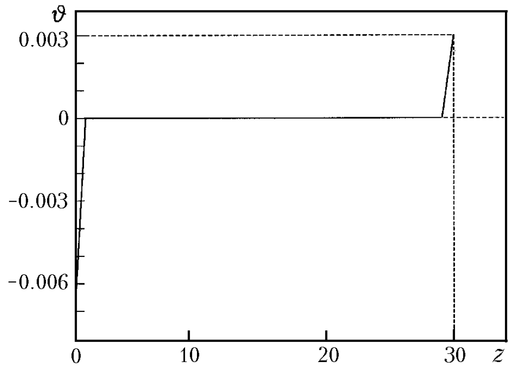
or

$$\left.\frac{\partial p}{\partial z}\right|_{z=z_0} = 0 \,, \;\; p \,|_{z=0} = p_0 \,; \tag{33}$$

the initial condition is $\vartheta(z, 0) = 0$.

Generally speaking, the form of the rheological relation is unknown, since the assumption of the elastic character of the reaction to the load applied holds true only of small strains of the medium. Therefore, we assume that the transport porosity of the medium is low, so we may assume that $m = 0$ (this holds true of many cases, for example, of such natural swelling systems as clays). Since one variable in system (25)–(31) has been determined, one equation becomes extraneous. Let Eq. (26) be such an equation. Furthermore, we note that the dependence of the filtration rate on the pressure gradient (28) is simplified. Next, we solve the problem numerically. In both problems (for boundary conditions of the first and second kind (32) and (33) respectively), we have used an explicit difference scheme. In the second problem (i.e., for boundary condition of the second kind (33) at entry into the layer), we have used the marching method to find the pressure profile. The calculation results are presented in Fig. 1.

Analysis of the Results. Since there are no experimental data on the pressure and shrinkage distribution in the layer strained (these data must be determined in rheological experiments in parallel), the values of the model's parameters were selected for reasons of convenience of calculations; therefore, the conclusions of the section are qualitative in character. Variation of the values of the parameters did not change the form of the dependences obtained. The calculations have confirmed the expectations of physical character placed on the model. Thus, in our opinion, of great interest is the pressure profile for the case where boundary condition (32) is used. It is seen that a stationary zone in



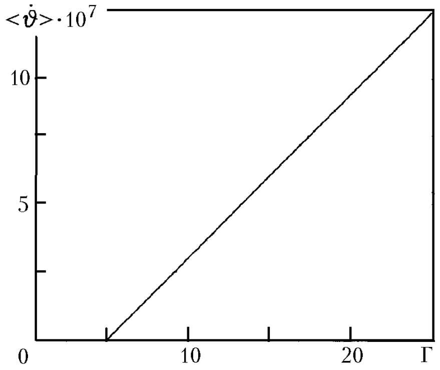


Fig. 2. Shrinkage profile in the layer. z, cm.

Fig. 3. Average shrinkage rate vs. applied load. Γ, kPa.

which flow is absent is formed in the central part of the layer. A flow arrives at this zone on the right and is removed on the left. The corresponding shrinkage distribution is shown in Fig. 2. It is seen that the zone of entry of the flow corresponds to the swelling zone (positive ϑ values), whereas the zone of removal of the flow (negative ϑ) corresponds to the shrinkage zone, so that the strain turns out to be nonuniform over the profile. It is of interest that the plots of shrinkage coincide for the two problems. The fact is that for the second case (condition (33)) water begins to be forced out from the layer. Whereas it has the plane from which to flow out at the left-hand boundary and a shrinkage zone is formed, at the right-hand boundary, conversely, water has no place to flow out and a swelling zone is formed. The plots of the average-over-the layer rate of shrinkage as a function of the load applied coincide for both cases, too (Fig. 3). It is seen that the character of the resulting curve corresponds to the Bingham rheology, which seems quite probable for swelling systems of the clay type [6]. It is noteworthy that the value of the limiting load on the layer, which physically ensures the absence of swelling of the entire layer, is linearly dependent on the value of the exchange capacitance e and the parameter α and is virtually independent of the permeability of the medium.

Conclusions. Problems including, in one form or another, the use of rheological models of swelling media such as clays or clay rocks are quite frequent in technology or engineering geology. As a rule, one immediately lays one hypothesis on the rheology of a medium, for example, the Bingham rheology, or another into such models. It was important for us to propose such a model of a medium that would rely on the known experimental facts referring to the properties of the medium (for example, the presence of osmotic pressure, leading to swelling, in the system) and would use a priori no assumptions on the rheology of the medium. Such a model was developed by combining the filtration-consolidation theory and the osmotic-cell model. Based on it, we have solved the simplest problem on shrinkage of a swelling layer under load and have shown that the model makes it possible to correctly describe the rheology of clays and clay rocks observed in experiments.

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NOTATION

$A^{(i)}$, work of internal surface forces; C, concentration of the electrolyte in transport pores; C_1 and C_2, concentration of the cations and anions in the solution; dS, area element, over which integration is carried out; dV, volume element; e, exchange capacitance of clay; e_{ij}, strain-rate tensor; F, free energy of the body with microdistortions; F_s, free energy of the solid skeleton phase; G_{ij}, external-load tensor; j, exchange flow between the skeleton and the transport pores; J_2', second invariant of the stress-tensor deviator; k, permeability of the medium; M_s, solid-phase mass; m, free (transport) porosity; n_{ij}, normal vector to the corresponding surface; $\mathbf{q}$, filtration rate; q, modulus of $\mathbf{q}$; $Q^{(e)}$, external heat; Q', uncompensated heat; p, pressure in the liquid phase; R, universal gas constant; T, temperature; t, time; S_s, solid-phase entropy; S_s^e, free surface of solid-phase particles; T_{ij}, deviator of the effective-stress tensor; U_s, internal energy of the solid phase; U_i, components of the vector of the displacement velocity of skeleton particles; V_0, representative volume; $V_0^{(0)}$, initial value of the representative volume of the medium; ∂V_0, boundary of the representative volume; V_s, solid-phase volume; $\mathbf{V}_f$, velocity of the fluid in transport pores; $\mathbf{V}_s$, solid-phase velocity; x, coordinate axis; z, vertical axis; z_0, clay-layer thickness; z_k, charge in the units of elementary charge of the corresponding ion (z_1, of the cation, z_2, of the anion); α, mass-exchange constant; Γ, modulus of external load; δ_{ij}, Kronecker delta symbol; ε_{ij}, strain tensor; η, viscosity of water; θ, shrinkage; $\dot{\theta}$, shrinkage rate; λ, μ, and ν, elastic constants; μ_k, chemical ionic potential in the solution; π, osmotic pressure; ρ_f, density of the fluid; ρ_s, density of the solid phase; ρ_w, density of water; σ_{ij}^{f}, effective-stress tensor; σ^{f}, trace of the effective-stress tensor; σ_{ij}^{s}, skeleton's true-stress tensor; σ, trace of the skeleton's true-stress tensor; Σ_s, total solid-phase surface; Σ_{s-f}, fluid-skeleton contact surface; τ_{ij}^{s}, deviator of σ_{ij}^{s}; Φ, electric potential. Subscripts and superscripts: 0, initial state; e, external part; (e), external heat; f, liquid phase; i and j, projections on the coordinate axis; (i), internal surface forces; k, corresponding ion of the solution (k = 1 and 2); n, normal component of the vector; s, solid phase (porous skeleton); w, water; $\cdot$, partial time derivative; $'$, deviator of the corresponding tensor, except for Q' (uncompensated heat); $\bar{\ }$, parameters belong to the pore solution, i.e., the solution as part of the medium's skeleton; 1, cation; 2, anion.

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